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REACTION OF 1,3-DIBROMO- AND 1,3-DICHLOROACETONE WITH 2-AMINOAZAHETEROCYCLES

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The reactions of 1,3-dibromoacetone with 2-aminoazines and 2-aminoazoles has been carried out for the first time and the pure intermediate quaternary salts have been isolated. They undergo cyclization to the corresponding imidazoazines and imidazoazoles containing a bromomethyl group. Similar condensations were carried out with 1,3-dichloroacetone.

Keywords: 1,3-dibromoacetone, 1,3-dichloroacetone, imidazo[1,2-*a*]pyridines, imidazo[1,2-*a*]-pyrimidines, imidazo[2,1-*b*]thiazoles.

The reaction of mono-α-halo ketones with 2-aminoazaheterocycles, suggested by Chichibabin [1], is one of the most suitable methods for the annelation of the imidazole ring and for the synthesis of imidazoheterocycles with a nitrogen atom at a ring junction. Nevertheless this reaction has been little studied for α,α'-dihalo ketones. There are only two known reports on the use of 1,3-dibromoacetone in similar condensations [2,3]. The use of 1,3-dichloroacetone is described in a number of papers [4-15].

We have studied the reaction of 1,3-dibromoacetone with 2-aminosubstituted pyridine, pyrimidine, thiazole, 1,3,4-thiadiazole and their derivatives. It was observed that when 1,3-dibromoacetone was heated with 2-aminopyridine in ethanol (the conditions in which mono-α-halo ketones normally react) complete resinification of the reaction mixture occurred, but if the reactants were dissolved at room temperature in ethyl acetate a white colorless product **1a** precipitated after some time. The other mentioned 2-aminoazaheterocycles reacted similarly. Depending on the nature of the heterocycle salts of type **1** (pyridine, pyrimidine) or type **2** (thiazole, thiadiazole) were formed. On short heating in acetic acid they were converted into salts **3**. 1,3-Dichloroacetone reacted considerably more slowly and with lower yields.

A salt of type **1** was first obtained from ω-bromoacetophenone and 2-aminopyridine. Its structure was confirmed by IR and UV spectroscopy [16]. In a study of the reaction of 2-aminopyridine with ω-bromoacetophenone, the authors [17] registered the appearance of a salt of type **1** in the sample tube by ^{1}H NMR spectroscopy. The salt appeared to be an intermediate reaction product which existed for a short time and was rapidly converted into the final product, 2-phenylimidazo[1,2-*a*]pyridine. The separation of products with similar structures was reported elsewhere [12, 14, 18].

Salts **1** and **2**, the structures of which were confirmed by IR and ^{1}H NMR spectroscopy and elemental analysis are not particularly stable in solution but they exist in the crystalline sate at room temperature (Tables 1 to 3). A characteristic feature of the ^{1}H NMR spectra of salts **1** is the presence of two doublets for the non-equivalent protons of the N^+–CH_2 group at 4.46-4.85 ppm (^2J = 14-15 Hz), while in the spectra of salts **2** the

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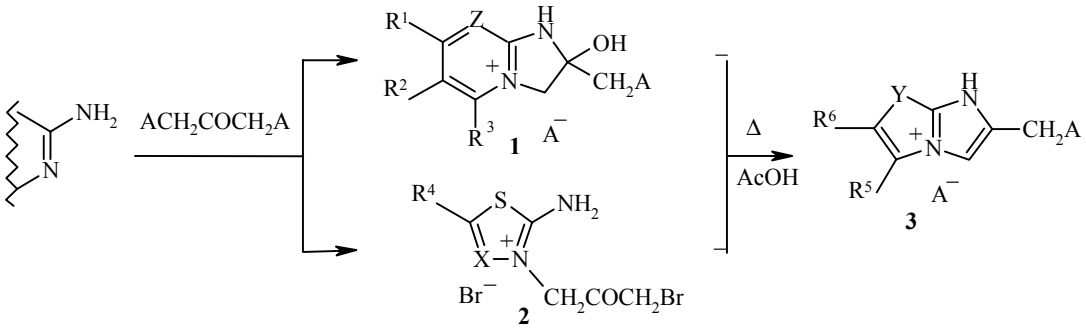


Compound*	R^1	R^2	R^3	Z	A	Compound	R^5	R^6	Y	A
1a	H	H	H	CH	Br	**3a**	H	H	CH=CH	Br
1b	H	H	H	CH	Cl	**3b**	H	H	CH=CH	Cl
1c	H	H	CH_3	CH	Br	**3c**	CH_3	H	CH=CH	Br
1d	H	H	CH_3	CH	Cl	**3d**	CH_3	H	CH=CH	Cl
1e	H	Cl	H	CH	Br	**3e**	H	Cl	CH=CH	Br
1f	H	Cl	H	CH	Cl	**3f**	H	Cl	CH=CH	Cl
1g	H	H	H	N	Br	**3g**	H	H	CH=N	Br
1h	H	H	H	N	Cl	**3h**	H	H	CH=N	Cl
1i	CH_3	H	CH_3	N	Br	**3i**	CH_3	H	$C(CH_3)$=N	Br
						3j	H	H	S	Br
						3k*[2]	CH_3	H	S	Br

* **2a** R^4 = H, X = CH; **2b** R^4 = CH_3, X = N; **a, b** A = Br. Salt **2b** was not converted into a salt of type **3**.

*[2] In the reaction of 2-amino-4-methylthiazole with 1,3-dibromoacetone the ^{1}H NMR spectrum indicated the formation of a mixture of salts of types **1-3** in approximately equal amounts, but on heating of this mixture in acetic acid salt **3k** was obtained.

same group gives a singlet at 5.42-5.49 ppm. Furthermore, separate singlets are observed for the protons of the OH and NH groups, whereas only one two-proton singlet for the NH_2 group is observed for the salts **2**. The IR spectra of salts **2** show absorption bands for $\nu_{C=O}$ at 1680-1700 and for ν_{NH_2} at 3300-3100 cm^{-1}, while the $\nu_{C=O}$ band is absent in the spectra of salts **1**.

TABLE 1. Characteristics of the Compounds Synthesized*

Compound*[2]	Empirical formula	Found, % / Calculated, %			mp, °C*[3]	Yield, %
		C	H	N		
1	2	3	4	5	6	7
1b	$C_8H_{10}Cl_2N_2O$	43.22 / 43.46	4.51 / 4.56	12.54 / 12.67	—	72
1d	$C_9H_{12}Cl_2N_2O$	45.72 / 45.98	5.06 / 5.14	11.75 / 11.91	—	68
1e	$C_8H_9Br_2ClN_2O$	27.78 / 27.90	2.58 / 2.63	8.02 / 8.13	—	91
1f	$C_8H_9Cl_3N_2O$	37.34 / 37.60	3.47 / 3.55	10.82 / 10.96	—	65

TABLE 1 (continued)

1	2	3	4	5	6	7
1h	$C_7H_9Cl_2N_3O$	37.54 37.86	4.01 4.08	18.76 18.92	—	58
1i	$C_9H_{13}Br_2N_3O$	31.67 31.88	3.78 3.86	12.18 12.39	—	87
2b	$C_6H_9Br_2N_3OS$	15.06 15.23	1.88 1.92	8.79 8.88	—	71
3d	$C_9H_{10}Cl_2N_2$	49.58 49.79	4.57 4.64	12.77 12.90	187 (Acetic acid)	81
3e	$C_8H_7Br_2ClN_2$	29.32 29.44	2.11 2.16	8.52 8.58	204 (Acetic acid)	88
3f	$C_8H_7Cl_3N_2$	40.32 40.46	2.88 2.97	11.65 11.79	191 (Acetic acid)	78
3i	$C_9H_{11}Br_2N_3$	33.45 33.67	1.98 2.03	9.29 9.40	252 (Acetic acid)	87
3k	$C_7H_8Br_2N_2S$	26.79 26.95	2.50 2.58	8.89 8.98	176 (Acetic acid)	76
4c	$C_9H_9BrN_2$	47.69 48.03	3.94 4.03	12.31 12.45	195 (Cyclohexane)	80
4d	$C_9H_9ClN_2$	59.72 59.84	4.95 5.02	15.40 15.51	133 (Acetonitrile)	69
4e	$C_8H_6BrClN_2$	38.96 39.14	2.42 2.46	11.55 11.41	120 (Isopropanol)	87
4f	$C_8H_6Cl_2N_2$	47.63 47.79	2.93 3.01	13.81 13.93	119 (Ethanol)	78
4i	$C_9H_{10}BrN_3$	44.87 45.02	4.15 4.20	17.37 17.50	234 (Clorobenzene)	62
5a	$C_{16}H_{14}Br_2N_4$	45.32 45.53	3.29 3.34	13.43 13.27	242 (Acetic acid)	71

* Characteristics of compounds **1a**,**c**,**g**, **2a**, **3a**,**c**,**g** are cited in [2], **3b** in [5, 10], **3h** in [11, 14], **4a**,**g** in [3]. **4b** in [4, 5, 10], and **4h** in [10, 13, 14].

*[2] Melting points were not determined for compounds **1b**,**d-f**,**h,i,** and **2b** because of ease of dehydration.

*[3] Solvents are given in brackets.

Salts **1** and **2** were obtained in good yields and often in analytically pure state. They are colorless crystalline substances, soluble in water, easily dehydrated and are therefore not storable for long periods. When heated for a short while in glacial acetic acid salts **1** and **2** are converted into salts **3**. The latter are soluble in water and are converted into the imidazoheterocycles **4** under the influence of bases (sodium carbonate, sodium bicarbonate, or aqueous ammonia). The corresponding bases were not obtained from salts **3j,k**.

Compounds **4a-i** are soluble in chloroform and acetone. The bases with chloromethyl groups are quite stable, whereas the bromomethyl derivatives, especially in the case of imidazo[1,2-*a*]pyridine, were converted over several days into salt-like products the structure of which was not established. The possibility of self-alkylation of these bases was confirmed by the formation of the salt **5a**, the structure of which was confirmed by ^{1}H NMR spectroscopy and elemental analysis, on heating of 2-(bromomethyl)imidazo[1,2-*a*]pyridine (**4a**) in isopropanol for a short time.

TABLE 2. ^{1}H NMR Spectra of Compounds **1**, **3**, **4** and **5a**

Com-pound	Chemical shifts, δ, ppm, and coupling constants, *J* (Hz)									
	3-H, s	5-H	6-H	7-H	8-H	CH_2–N^+, d	CH_2Hal, s	OH	NH	Other signals
1	2	3	4	5	6	7	8	9	10	11
1a	—	8.42, d, $^{3}J_{H5,H6}$ = 6.5	7.12, dd	8.11, dd, $^{3}J_{H6,H7}$ = 6.7, $^{3}J_{H7,H8}$ = 8.6	7.18, d	4.65, 4.85, $^{2}J_{H,H}$ = 15	3.89	10.21, s*	7.55, br. s*	—
1b	—	8.38, d, $^{3}J_{H5,H6}$ = 6.5	7.02, dd	8.02, dd, $^{3}J_{H6,H7}$ = 6.7, $^{3}J_{H7,H8}$ = 8.6	7.14, d	4.59, 4.78, $^{2}J_{H,H}$ = 14.7	3.97	10.48, s*	7.90, br. s*	—
1c	—	—	6.92, d	7.93, dd, $^{3}J_{H6,H7}$ = 6.7, $^{3}J_{H7,H8}$ = 8.6	7.00, d	4.50, 4.76, $^{2}J_{H,H}$ = 14.6	3.85	10.08, s*	7.42, br. s*	2.48, s (CH_3)
1d	—	—	6.90, d	7.95, dd, $^{3}J_{H6,H7}$ = 6.4, $^{3}J_{H7,H8}$ = 8.6	6.98, d	4.57, 4.74, $^{2}J_{H,H}$ = 14.5	3.99	10.38, s*	7.80, br. s*	2.52, s (CH_3)
1e	—	8.78, d, $^{4}J_{H5,H7}$ = 1.4	—	8.22, dd, $^{3}J_{H7,H8}$ = 8.6	7.20, d	4.58, 4.82, $^{2}J_{H,H}$ = 14.7	3.88	10.42, s*	7.52, br. s*	—
1f	—	8.73, d, $^{3}J_{H5,H6}$ = 6.5	—	8.12, dd, $^{3}J_{H6,H7}$ = 6.4, $^{3}J_{H7,H8}$ = 8.6	7.18, d	4.56, 4.75, $^{2}J_{H,H}$ = 14.2	4.01	10.70, s*	7.52, br. s*	—
1g	—	8.93, d, $^{3}J_{H5,H6}$ = 6.3	7.25, dd	8.89, d, $^{3}J_{H6,H7}$ = 4.7	—	4.58, 4.81, $^{2}J_{H,H}$ = 14.4	3.86	11.03, s*	7.60, br. s*	—
1h	—	8.96, d, $^{3}J_{H5,H6}$ = 6.3	7.21, dd	8.88, d, $^{3}J_{H6,H7}$ = 4.7	—	4.68, 4.72, $^{2}J_{H,H}$ = 14.1	3.96	11.09, s*	7.62, br. s*	—
1i	—	—	7.04, s	—	—	4.46, 4.68, $^{2}J_{H,H}$ = 14	3.79	10.74, s*	7.44, br. s	2.46, s, 2.50, s (CH_3)
3a	8.57	9.07, d, $^{3}J_{H5,H6}$ = 6.5	7.53*^{2}, m	8.02*^{2}, m	8.02*^{2}, m	—	5.02	—	9.53*^{3}	—
3b	8.52	9.01, d, $^{3}J_{H5,H6}$ = 6.5	7.46*^{2}, m	7.95*^{2}, m	7.95*^{2}, m	—	5.09	—	9.05*^{3}	—
3c	8.50	—	7.44*^{2}, m	7.92*^{2}, m	7.92*^{2}, m	—	5.02	—	8.80*^{3}	2.78, s (CH_3)
3d	8.43	—	7.38*^{2}, m	7.88*^{2}, m	7.88*^{2}, m	—	5.10	—	8.95*^{3}	2.76, s (CH_3)

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10	11
3e	8.42	9.30, s	—	7.95, s	7.95, s	—	4.93	—	6.24*[3]	—
3f	8.42	9.30, s	—	7.90, s	7.90, s	—	5.06	—	13.20*[3]	—
3g	8.48	9.48, dd, $^3J_{H5,H6}$ = 6.5; $^4J_{H5,H7}$ = 2	7.67, dd	9.10, dd, $^3J_{H7,H6}$ = 4.4	—	—	4.95	—	12.8*[3]	—
3h	8.43	9.42, dd, $^3J_{H5,H6}$ = 6.7; $^4J_{H5,H7}$ = 2	7.58, dd	8.97, dd, $^3J_{H7,H6}$ = 4.4	—	—	5.07	—	7.42*[3]	—
3i	8.38	—	7.52, s	—	—	—	4.93	—	9.53*[3]	2.67, s, 2.76, s (CH_3)
4a	7.66	8.09, d, $^3J_{H5,H6}$ = 6.5	6.82, dd	7.23, dd, $^3J_{H7,H8}$ = 8.7, $^3J_{H7,H6}$ = 6.8	7.61, d	—	4.69	—	—	—
4b	7.62	8.07, d, $^3J_{H5,H6}$ = 6.6	6.80, dd	7.21, dd, $^3J_{H7,H8}$ = 8.8, $^3J_{H7,H6}$ = 6.7	7.57, d	—	4.78	—	—	—
4c	7.52	—	6.62, d	7.18, dd, $^3J_{H7,H8}$ = 8.2, $^3J_{H7,H6}$ = 6.8	7.48, d	—	4.69	—	—	2.56, s (CH_3)
4d	7.53	—	6.63, d	7.20, dd, $^3J_{H7,H8}$ = 8.8, $^3J_{H7,H6}$ = 6.5	7.50, d	—	4.81	—	—	2.60, s (CH_3)
4e	7.95, s	8.61, d, $^4J_{H5,H7}$ = 1.6	—	7.24, dd, $^3J_{H7,H8}$ = 8.6	7.53, d	—	4.72	—	—	—
4f	7.98, s	8.66, d, $^4J_{H5,H7}$ = 1.4	—	7.27, dd, $^3J_{H7,H8}$ = 8.6	7.55, d	—	4.81	—	—	—
4g	7.93, s	8.88, dd, $^3J_{H5,H6}$ = 6.4; $^4J_{H5,H7}$ = 1.8	7.04, dd	8.56, dd, $^3J_{H7,H8}$ = 4.4	—	—	4.74	—	—	—
4i	7.43, s	—	6.59, s	—	—	—	4.67	—	—	2.57, s (CH_3)
5a	8.44, s	8.78, d, $^3J_{H5,H6}$ = 6.8	7.67*[2], m	8.25, d, $^3J_{H8,H7}$ = 8.2	8.15 d	6.22, s	—	—	—	—

* Exchanges with D_2O.

*[2] Center of multiplet.

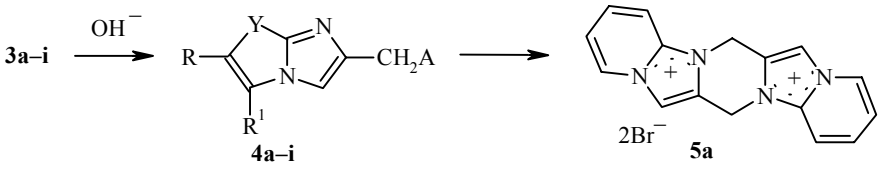
*[3] Broad signal, overlapping with the water signal of the solvent as indicated from the integration curve of the ^1H NMR spectrum.

TABLE 3. ^{1}H NMR Spectra of Salts **2**, **3j**, and **3k**

Compound	Chemical shifts, δ, ppm; coupling constants, *J* (Hz)								
	2-H	3-H	4-H	5-H	NH_2, s	CH_2–N^+, s	CH_2Br, s	NH	other signals
2a	—	—	7.06, d, $^3J_{H4,H5}$ = = 4.4	7.32, d	9.64*	5.42	4.56	—	—
2b	—	—	—	—	10.02*	5.49	4.58	—	2.54, s (CH_3)
3j	7.70, d, $^3J_{H2,H3}$ = = 4.1	8.26, d	—	8.29, s	—	—	4.93	8.02*[2]	—
3k	7.36, s	—	—	8.31, s	—	—	4.92	8.60*[2]	2.51, s (CH_3)

* Exchanged with D_2O.

*[2] Broad signal, overlapping with the water signal of the solvent as indicated from the integration curve of the ^{1}H NMR spectrum.



Compound	R	R^1	Y	A	Compound	R	R^1	Y	A
4a	H	H	CH=CH	Br	**4f**	Cl	H	CH=CH	Cl
4b	H	H	CH=CH	Cl	**4g**	H	H	CH=N	Br
4c	H	CH_3	CH=CH	Br	**4h**	H	H	CH=N	Cl
4d	H	CH_3	CH=CH	Cl	**4i**	H	CH_3	C(CH_3)=N	Br
4e	Cl	H	CH=CH	Br					

So we have developed a simple and useful method for the preparation of imidazopyridines, imidazopyrimidines, and imidazothiazoles containing bromo- or chloromethyl groups in the imidazole nucleus and we have confirmed the mechanism for the Chichibabin reaction proposed previously [17].

EXPERIMENTAL

^{1}H NMR spectra were recorded on a WP-100SY (100 MHz) spectrometer in DMSO-d_6 for salts **1-3**, in CF_3COOD for **5a**, in $(CD_3)_2CO$ for **4e**,**f**,**g**, and in $CDCl_3$ for **4a-d**,**h-i** (TMS as internal standard). IR spectra were recorded on a Pye-Unicam SP3-300 spectrophotometer in KBr tablets.

General Method for the Synthesis of Salts 1 and 2. 1,3-Dibromo- or 1,3-dichloroacetone (0.01 mol) in ethyl acetate (5-10 ml) was added with stirring to a solution of the corresponding 2-aminoheterocycle (0.01 mol) in ethyl acetate (10-50 ml) and the mixture was kept for 2-5 days. The precipitate was filtered off, washed with acetone and ether, and dried in the air to give 2-(bromomethyl)-2-hydroxy-1H,2H,3H-imidazo-[1,2-*a*]pyridinium (**1a**), 2-(bromomethyl)-2-hydroxy-5-methyl-1H,2H,3H-imidazo[1,2-*a*]pyridinium (**1c**), 2-(bromomethyl)-6-chloro-2-hydroxy-1H,2H,3H-imidazo[1,2-*a*]pyridinium (**1e**), 2-(bromomethyl)-2-hydroxy-1H,2H,3H-imidazo[1,2-*a*]pyrimidinium (**1g**), 2-(bromomethyl)-2-hydroxy-5,7-dimethyl-1H,2H,3H-imidazo-

[1,2-*a*]pyrimidinium (**1i**), 2-amino-3-(3-bromo-2-oxoprop-1-yl)thiazolium (**2a**), and 2-amino-3-(3-bromo-2-oxoprop-1-yl)-5-methyl-1,3,4-thiadiazolium (**2b**) bromides, and 2-(chloromethyl)-2-hydroxy-1H,2H,3H-imidazo[1,2-*a*]pyridinium (**1b**), 2-hydroxy-2-(chloromethyl)-5-methyl-1H,2H,3H-imidazo[1,2-*a*]pyridinium (**1d**), 6-chloro-2-(chloromethyl)-2-hydroxy-1H,2H,3H-imidazo[1,2-*a*]pyridinium (**1f**), and 2-(chloromethyl)-2-hydroxy-1H,2H,3H-imidazo[1,2-*a*]pyrimidinium (**1h**) chlorides.

General Method for the Synthesis of Salts 3a-j. A solution of salts **1a-i** or **2a** (0.01 mol) in glacial acetic acid (10-20 ml) was heated with stirring for 15-30 min at 80-100°C. The precipitate which separated on cooling was filtered off, washed with a small quantity of acetic acid, then with acetone and ether, to give 2-(bromomethyl)-1H-imidazo[1,2-*a*]pyridinium (**3a**), 2-(bromomethyl)-5-methyl-1H-imidazo[1,2-*a*]pyridinium (**3c**), 2-(bromomethyl)-6-chloro-1H-imidazo[1,2-*a*]pyridinium (**3e**), 2-(bromomethyl)-1H-imidazo[1,2-*a*]-pyrimidinium (**3g**), 2-(bromomethyl)-5,7-dimethyl-1H-imidazo[1,2-*a*]pyrimidinium (**3i**), and 6-(bromomethyl)-7H-imidazo[2,1-*b*]thiazol-4-ium (**3j**) bromides, and 2-(chloromethyl)-1H-imidazo[1,2-*a*]pyridinium (**3b**), 2-(chloromethyl)-5-methyl-1H-imidazo[1,2-*a*]pyridinium (**3d**), 6-chloro-2-(chloromethyl)-1H-imidazo[1,2-*a*]-pyridinium (**3f**), and 2-(chloromethyl)-1H-imidazo[1,2-*a*]pyrimidinium (**3h**) chlorides.

6-(Bromomethyl)-3-methyl-7H-imidazo[2,1-*b*]thiazolium bromide (**3k**) was obtained as described on p. 591.

General Method for the Synthesis of Bases 4. A solution of salts **3a-i** (0.01 mol) in water (10-20 ml) was neutralized with sodium bicarbonate solution. The precipitate was filtered off, washed with water, squeezed out, and dried in the air to give 2-(bromomethyl)imidazo[1,2-*a*]pyridine (**4a**), 2-(chloromethyl)imidazo[1,2-*a*]-pyridine (**4b**), 2-(bromomethyl)-5-methylimidazo[1,2-*a*]pyridine (**4c**), 2-(chloromethyl)-5-methylimidazo[1,2-*a*]-pyridine (**4d**), 2-(bromomethyl)-6-chloroimidazo[1,2-*a*]pyridine (**4e**), 6-chloro-2-(chloromethyl)imidazo[1,2-*a*]-pyridine (**4f**), 2-(bromomethyl)imidazo[1,2-*a*]pyrimidine (**4g**), 2-(chloromethyl)imidazo[1,2-*a*]pyrimidine (**4h**), and 2-(bromomethyl)-5,7-dimethylimidazo[1,2-*a*]pyridine (**4i**).

7H,15H-Dipyrido[2',1':2,3]imidazo[1,5-*a*:1,5-*a*]pyrazin-5,13-diium Dibromide (5a). A solution of **4a** (0.01 mol) in isopropanol (5 ml) was refluxed for 20 min. The crystals which formed on cooling were washed with isopropanol and ether.

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